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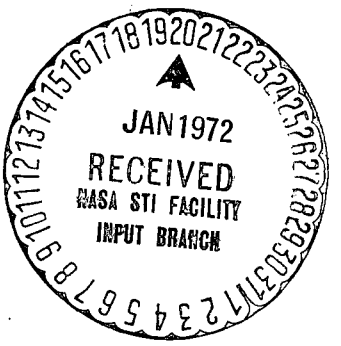

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CONTINUOUS MANUFACTURE OF PHTHALATES FROM PHTHALIC ANHYDRIDE AND HIGH BOILING ALCOHOLS

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ABSTRACT: This article describes a modern commercial synthesis of phthalates which produces 100,000 tons per year in continuous operation. This process yields 98% of the theoretical maximum, based on both phthalic anhydride and ethylhexanol. BASF uses this method for 90-95% of its total plasticizer production.

INTRODUCTION

A modern commercial synthesis of phthalates is described, an example of which is a continuous operation apparatus for the production of dioctyl phthalate with a capacity of 100,000 tons per year. The yield amounts to 98% of the theoretical based on both phthalic anhydride and on ethylhexanol. By /971* the exclusive use of phthalic anhydride and alcohols as the starting materials, one obtains a simple separation operation for the purification step of the process and at the same time obtains plasticizers of outstanding quality. In the autocatalytic esterification of anhydrides with alcohols, both the usual use of strong acids as a catalyst and inert materials as solvents can be eliminated. The synthesis is carried out in a cascade reaction and is generally applicable to high boiling alcohols. Under somewhat modified conditions, the preparation of esters of aliphatic dicarboxylic acids with alcohols was also carried out. The procedure is flexible with respect to apparatus breakdown and quality fluctuations of the starting materials. In this way the most efficient esterification is presented - a compromise between reaction time and purification expenses. At BASF, 90-95% of the total plasticizer production is prepared by this method.

Phthalates have been known as plasticizers since 1900 [1]. At first they were used in place of camphor in celluloid. Later, with the rise of polyvinyl chloride (PVC), phthalates were among the main group of plasticizers. Today their percentage of the market amounts to 65-70%. Of all the different phthalates only 50%, the bis-(2-ethylhexyl) phthalates, known as dioctyl phthalates, known as dioctyl phthalates (DOP), exhibit a compromise of

*Numbers in margin indicate pagination in foreign text.

properties, such as solvent effect and volatility, applicable to plasticizers. The dioctyl phthalates constitute 33% of all the plasticizers.

At BASF, in 1908, dimethyl phthalate was produced for the first time. In 1940, the production of dioctyl phthalate came into effect. During the course of a quarter of a century, especially in connection with the rapid development of PVC, the production of DOP by BASF reached an order of magnitude which makes conversion from a batch process to a continuous process an urgent matter. Also, the increasing requirements on plasticizer quality make a continuous process evident. The higher the quality of the ester, the more versatile is its use. Thus the phthalate should be colorless (color number according to Hazen <40 to 50). In addition, an acid number of $\leqslant 0.10$ must be guaranteed since an excessive acidity detrimentally affects the color of the plastic; its deterioration accelerates and its specific resistance decreases. Finally, plasticizers which are to be used for electrotechnical purposes must have a correspondingly large dielectric strength. Therefore, even traces of electrolytes, such as water or alcohol must be removed. Also, a volatility value of $\leqslant 0.25\%$ must be observed. This high quality requirement leads to production difficulties, especially in the hitherto discontinuous process where occasional distinct decreases in quality result.

Special difficulties prescribe the purifications operations used. They include deacidification, washing, color clarification and the removal of volatile components which are determined in their scope of the synthesis method. Although continuous esterifications are described in the literature [2, 3], it was not until 1963 that our first technical operation went into effect. A continuous large scale process was already in use, however.

TECHNICAL STATUS

Acids are used as catalysts in the esterification of phthalic acid. Concentrated sulfuric acid, toluenesulfonic acid, sodium hydrogen sulfate and α-naphthalenesulfonic acid are used industrially [4]. A favorable displacement of the esterification equilibrium is obtained by continuous removal of the resulting water. In the esterification of phthalic anhydride with high boiling alcohols, a cyclic process is most often used today. The water is removed

azeotropically by either an inert water-insoluble organic substance such as toluene or by an excess of alcohol.

The main catalysts used force the imposition of an upper limit on the reaction temperature. According to B. Wolff [3], the esterification of phthalic anhydride with alcohols ($> C_4$) in the presence of sulfuric acid must not exceed 140°C in order to avoid color in the product. Under appropriate conditions, operating temperatures up to 165°C can be used without a decrease in quality. However, to be sure, the acid catalyzed dehydration of ethylhexanol is observed as a side reaction. At an increase of temperature to about 175° to 200°C, the reaction rate increases, therefore, allowing for an increased rate of quality deterioration due to faster and more side reactions, for example, acid catalyzed ether formation. At higher temperatures, the main esterification reaction is distinctly superimposed with side reactions such as alcohol dehydration, isomerization and other formation [5]. Correspondingly, unsaturated alcohols and diene derivatives of the ethylhexanol have been analytically detected. Moreover, p-toluenesulfonic acid reacts with the solvent toluene under these conditions to give p-ditoluyl sulfone which remains dissolved in the ester [6].

These side reactions are also observed to a lesser degree at lower temperatures [7]. In order to reduce them, selective catalysts such as organo-metallic compounds were suggested [8]. However, most are less active and therefore must be used in large quantitites.

In every case, the expenditure for purification of the crude ester is considerable. Thus, among others, an alkaline steam distillation is used to improve the ester color [9]. The most efficient purification and color clarification must be obtained through the expensive distillation of the ester at 1 Torr [3]. Frequently, oxidation with, for example, hydrogen peroxide or adsorption on activated charcoal is used. On this basis, the most economical esterification is therefore a compromise between reaction time and purification expenditure. Therefore, today almost everyone uses p-toluenesulfonic acid as the catalyst and operates extensively under similar conditions. This esterification must be carried out continuously, therefore a separate separation step is built into the 2-ethylhexanol and toluene cycles. Furthermore, the recovered unreacted starting material must be carefully purified of any side products since

the type and amount of side product greatly influences the course of the reaction, as in the case of the discontinuous process. With this, the repeated recoveries cause no difficulties since a smaller part of the stirred component can be always separated.

MECHANISM AND KINETICS

In the formation of neutral phthalates, the monoester is first formed in a bimolecular reaction of phthalic anhydride and 2-ethylhexanol. The reaction is exothermic and the equilibrium is displaced far in favor of ester formation. The carboxyl group of the monoester is then esterified in a second step. In the presence of acid catalysts both reactions are catalyzed by protons [10]. Kinetic investigations have shown that the formation of diesters from monoesters is the slowest and thus the rate determining step. For a not too high extent of reaction, the experimental results can be represented as a first order reaction, that is, a pseudomonomolecular reaction. The temperature dependence of the reaction indicates that the activation energy is 17 kcal/mole. The total heat of reaction for both reaction steps amounts to 20 kcal/mole.

AUTOCATALYTIC REACTION

Fundamentally, monophthalates can be esterified with 2-esthylhexanol by the autocatalytic action of the dissociating proton. Due to the relatively low hydrogen ion concentration, which determines the position of the ester equilibrium, a longer reaction time is necessary.

Without additional catalyst, the formation of the monester involves a nucleophilic alcoholysis of the anhydride which follows an SN_2 mechanism. The alcohol, therefore, serves as a Lewis base. The autocatalytic esterification therefore deviates from the usual mechanism in the first reaction step. The second reaction step in the autocatalytic formation of diphthalates in a second order reaction in which both the concentrations of the monoester and the proton decrease. In esterifications with added catalyst an essentially first order reaction results. Thus it must be investigated if an autocatalytic reaction would be useful in a continuous process.

As is known, the transfer of a first order reaction in a batch process to a continuously operating cascade of reactors is simple to calculate [11]. For

second order reactions, this question must be investigated. The results, which show the superiority of the autocatalytic reaction, move us to abandon the esterification process which was used until now. Meanwhile, the reaction time for a higher order reaction in a cascade reactor can be calculated [12].

Such a control calculation was somewhat confirmed by the conditions of the practical transfer of this reaction into industrial equipment. Since mineral acids are not necessary in the autocatalytic reaction, all the side reactions caused by them are simultaneously avoided. Furthermore, the upper temperature limit of 165° can be raised without deterioration of the ester quality by use /973 of the autocatalytic reaction. The reaction is then carried out at normal pressures at the boiling point of ethylhexanol (183,5°C), whereby toluene is not needed as the solvent. The water formed in the reaction can be removed by azeotropic distillation with the excess 2-ethylhexanol present. The procedure allows for the use of the excess alcohol without further direct purification. Decided simplification was obtained in the continuous process. The toluene cycle, the catalyst, the activated charcoal treatment for color classification are all eliminated. The reaction partners are only phthalic anhydride and 2-ethylhexanol.

On transfer to a large volume reactor of a 2000 ton/month operation unit, it is shown, to be sure, that a change from a smaller to a larger unit is not forthwith possible. Differences in their capacities and parameters which are not fully determined, such as extent of mixing and extent of water removal with respect to the stirring rate, influence the reaction course directly. With the further development of an 8500 ton/month unit, this was again confirmed.

SYNTHESIS CONDITIONS

Figure 1 shows the diagram of an industrial plant. The continuous esterification is carried out in a six-stage cascade reactor (a). Thereby, a sufficient reaction rate for di-2-ethylhexyl phthalate is attained in the cascade reactor at a temperature of from 185 to 205°C. The mole ratio of phthalic anhydride to 2-ethylhexanol in the cascade is 1:2.5. The water which is produced is removed at every stage by azeotropic distillation (b) with an excess of 2-ethylhexanol. The alcohol is returned directly into the cycle. The crude ester, which leaves the last reactor, is expanded in the vacuum at (c) and is thereby largely freed

of the excess ethylhexanol by evaporation. It is then neutralized in a vessle (d) with 3 to 5% caustic soda. In another vessel (e) traces of alkali are removed from the neutral crude ester by washing with water. Finally, the more volatile portion is quantitatively separated in an evaporation column (f) under reduced pressure. The neutral phthalate is then passed through a coarse filter (g) to eventually remove the existing impurities mechanically. The 2-ethylhexanol which accumulates from the alcohol distillation column (c) and from the evaporator column (f) returns, likewise without further purification, together with the ethylhexanol from the azeotropic water removal, into the cascade reactor. The spent liquor from the neutralization column (d), which contains the unreacted monophthalate as the sodium salt, is acidified with sulfuric acid. The freed monoester is washed and sent into the cascade reactors without purification.

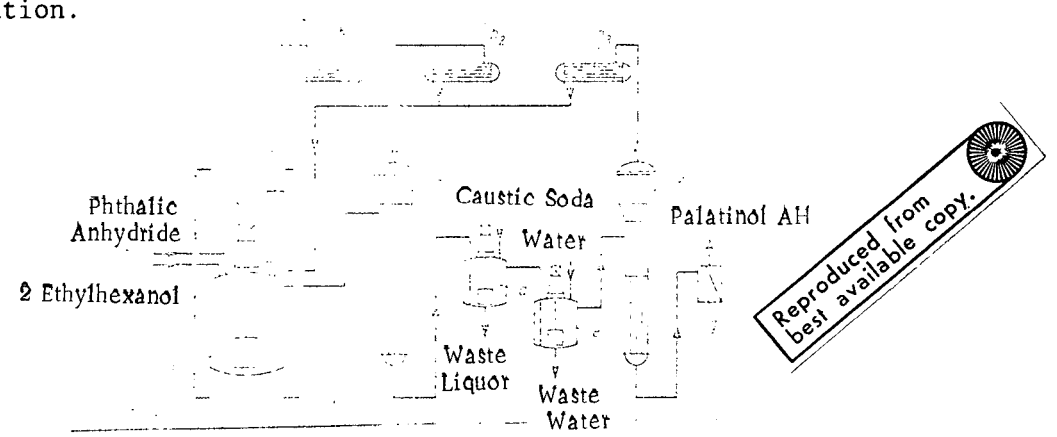

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Figure 1. Diagram of a Continuous Esterification Plant. (a) Six-stage cascade reactor (n = 6); (b) azeotropic distillation; (c) evaporator for alcohol separation; (d) neutralization; (e) washing; (f) evaporation; (g) filtration, h_1, h_2, h_3 - separators.

The increase of the reaction temperature to 185-205°C allows an especially favorable energy utilization in the continuous operation. The alcohol in the first stage is heated so much on the heat exchanger that the half-ester forms quickly on contact with the liquid phthalic anhydride, whereby the alcohol comes to a boil. The heat liberated on alcoholysis of the phthalic anhydride is sufficient for the formation of the diphthalate and a 75% conversion of the monoester is obtained. At every stage of the cascade reactor, the reaction

water is removed by distillation. However, only in the first stage is heat liberated. The heat of evaporation for the water in the later stages must be supplied from outside.

The phthalate obtained is very pure and has a Hazen color number of 10 to 20. Neither a rectification of the phthalate, nor a chemical bleaching with hydrogen peroxide, nor UV radiation or an activated charcoal treatment is necessary. In spite of this, it is expedient to provide for an adsorption treatment with activated charcoal in order to utilize a further not too underrated value of this process, namely, the flexibility with respect to quality fluctuation of the crude product. In larger scale production, one must calculate that the starting material deviates temporarily from its average quality on operational shutdowns. Due to this, impurities which lead to an ester which has only secondary quality are introduced. Then a color clarification cannot be avoided.

At a 97% conversion of the monophthlate to diphthalate in the multistage cascade reactor, a yield of 98% of the theorectical is obtained (based on both phthalic angydride as well as alcohol).

With a total supply of phthalic anhydride and 2-ethylhexanol of about 12.25 tons/hr, 100,000 tons/year of dioctyl phthalate is produced.

The production of "Palantinol AH", the principal trade mark of the plasticizer program of BASF, was 1 ton/year in 1940. Today 8500 ton/month are produced. In addition to the pure raw materials phthalic anhydride and 2-ethylhexanol only dilute caustic soda is needed.

FLEXIBILITY AND INDUSTRIAL EFFICIENCY

Autocatalytic esterification is also used at BASF for the reaction of phthalic anhydride with other alcohols such as iso-octanol, iso-nonanol, and iso-decanol [13]. It was used under some-what modified conditions in the production of esters of aliphatic dicarboxylic acids with alcohols. This method thus proves to be generally useful and efficient. It is known the operations were carried out at atmospheric pressure and in a cascade of reactors which, in comparison to other industrial procedural possibilities, has a relatively large reaction volumes in every reactor. In spite of the larger

reaction times, the best product is produced. In addition, the new procedure proves to be extraordinarily flexible towards work shutdowns. At BASF, 90-95% of the present plasticizer production is produced by this method.

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